



Comparative study of electrolyte additives using electrochemical impedance spectroscopy on symmetric cells

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HIGHLIGHTS

- Impedance spectroscopy on symmetric cells is used to determine which electrodes additives influence most.
- Almost all additives increase the negative electrode impedance.
- Almost all additives decrease the positive electrode impedance.
- Additives studied include VC, FEC, TMOBX, LiTFSI and water and their combinations.
- The impact of these additives on coulombic efficiency was also measured.

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ABSTRACT

The effect of various electrolyte additives and additive combinations added to a 1 M LiPF₆ EC:EMC electrolyte on the positive and negative electrodes surface of 1 year old wound LiCoO₂/graphite cells and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite cells was studied using electrochemical impedance spectroscopy (EIS) on symmetric cells. The additives tested were: vinylene carbonate (VC), trimethoxyboroxine (TMOBX), fluoroethylene carbonate (FEC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and H₂O alone or in combination. In general, compared to control electrolyte, the additives tested reduced the impedance of the positive electrode and increased the impedance of the negative electrode with the exception of LiTFSI in Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite wound cells. Higher charge voltage led to higher positive electrode impedance, with the exception of 2%VC + 2% FEC, and 2% LiTFSI. In some cases, some additives when mixed with another controlled the formation of the SEI at one electrode, and shared the formation of the SEI at one electrode when mixed with a different additive.

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1. Introduction

Li ion batteries have high gravimetric and volumetric energy densities, which make them suitable for transport applications. However parasitic reactions between the electrolyte and the electrodes limit their lifetime. The addition of additives to the electrolyte can in some cases lead to extended lifetime as shown by Broussely et al. [1] and to better rate performances [2,3].

Even if these additives are now widely used in the Li-ion battery industry, the details of how they work are poorly understood. For example, VC was thought to be a good additive for the formation of

an efficient solid electrolyte interface (SEI) at the negative electrode, which has been recently questioned [4,5,6]. It is now believed by some that the major beneficial impact of VC is at the positive electrode.

In an effort to better understand the role of these additives several research groups have dedicated substantial amounts of resources to their study [7–10]. For example, Burns et al. [3,5] used high precision coulometry, automated storage and electrochemical impedance spectroscopy (EIS) to evaluate the effect of additives on the cycling performances of commercial wound LiCoO₂/graphite and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂/graphite cells. Amongst other things, they showed that VC reduces the rate of parasitic reactions at the positive electrode, that TMOBX leads to greater parasitic reaction at the positive electrode but lowers the impedance, that the mix of TMOBX and VC leads to a good balance between reduced rate of

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parasitic reactions at the positive electrode and reduced impedance leading to good overall cell performances (rate capability and capacity retention). However, the effect of these additives on the impedance of the positive and negative electrode was not determined.

In order to easily detect the effect of an additive at the positive electrode and negative electrode separately, a method based on electrochemical impedance spectroscopy of symmetric cells developed by Chen et al. [11] was recently introduced [12]. This technique allows one to extract the effect of an additive on the charge transfer resistance (R_{ct}) of the positive electrode and negative electrode. R_{ct} of each electrode can be related to the nature of the SEI on the positive and negative electrode. Comparing the R_{ct} of both electrodes allows the effect of an additive on the positive and negative electrode to be detected (if the products of the reactions are insoluble). This technique proved to be very useful in studying the effect of VC and TMOBX on both electrodes of wound LiCoO₂/graphite cells. Petibon et al. showed that VC greatly reduced R_{ct} of the positive electrode at both 1 wt% and 2 wt%, VC did not strongly effect R_{ct} of the negative electrode at 1 wt%, but greatly increased R_{ct} of the negative electrode at 2 wt%. They also showed that TMOBX does not strongly affect the negative electrode impedance but greatly reduces R_{ct} of the positive electrode when 0.3 wt% of TMOBX is used. Finally, Petibon et al. showed that when 2 wt% VC and 0.3 wt% TMOBX were introduced, the effect of VC at the negative electrode and the effect of TMOBX at the positive electrode were maintained.

In this paper similar studies to those of Petibon et al. [12] are reported for a relatively large set of additives studied over a period of more than two years. The additives, 2 wt% FEC, 2 wt% LiTFSI, 100 ppm H₂O and several pairs of additives in addition to 2 wt% VC and 0.3 wt% TMOBX have been studied to determine their effect on the R_{ct} of the positive and negative electrodes of wound Li [Ni_{0.4}Mn_{0.4}Co_{0.2}]/graphite cells (called NMC cells), and two groups of LiCoO₂/graphite cells charged to different cut-off voltages (called LV-LCO and HV-LCO cells). It is believed that this work will be of interest to scientists trying to improve the lifetime of Li-ion cells.

2. Experimental

Wound prismatic LiCoO₂/graphite and Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]/graphite cells with 1 M LiPF₆, EC:EMC (3:7 by weight) were used in this study. The cells studied contained approximately 1.5 g of electrolyte per gram of negative active material. Table 1 lists the additives tested in which cell chemistries. Some combinations were not tested due to unavailability of cells.

Fig. 1 shows the history of the cells used in this study. The cells were first subjected to an automated storage test [7]. This test consists of two discharge–charge cycles between the lower and upper voltage cut-off, followed by an open circuit storage step of 500 h at the top of charge. The two discharge–charge cycles and the open circuit voltage steps are then repeated one more time. The lower and upper voltage cut-offs of the NMC cells were 3.3 V and 4.225 V, respectively. Two groups of LiCoO₂/graphite cells were used. The lower and upper voltage cut-offs of the first group, called LV-LCO cells, were 3.4 V and 4.075 V, respectively. The lower and upper voltage cut-offs of the second group, called HV-LCO cells, were 3.4 V and 4.175 V, respectively. All cells contained the same graphite negative electrode and their negative to positive active material ratio was balanced according to their voltage cut-off. The ratios of the active mass of the positive electrode and the active mass of the negative electrode for the LV-LCO cells, HV-LCO, and NMC cells were 1.6, 1.4, and 1.2 respectively. After the automated storage test the cells were then put away for approximately one year at an open circuit voltage around 3.9 V at room temperature

Table 1

List of additives studied in this work.

Additive	NMC/graphite 4.225 V	LV LCO/graphite 4.075 V	HV LCO/graphite 4.175 V
Control	Yes	Yes	Yes
1%VC (Novolyte)	Yes	Yes	Yes
2% VC (Novolyte)	Yes	Yes	No
0.3% TMOBX (BASF 99.2%)	Yes	Yes	Yes
2% FEC (Novolyte)	Yes	Yes	Yes
2% LiTFSI (3 M, 99.9%)	Yes	Yes	Yes
100 ppm H ₂ O	No	Yes	No
2% VC + 0.3% TMOBX	Yes	Yes	Yes
2% VC + 2% FEC	Yes	Yes	Yes
2% VC + 2% LiTFSI	Yes	Yes	Yes
2% VC + 100 ppm H ₂ O	Yes	No	No
2% VC + 1000 ppm H ₂ O	No	Yes	No
2% VC + 2% LiTFSI	No	Yes	No
+ 100 ppm H ₂ O			
2% VC + 2% LiTFSI	Yes	Yes	No
+ 1000 ppm H ₂ O			
2% VC + 0.3% TMOBX	No	Yes	No
+ 100 ppm H ₂ O			

(19 °C–22 °C). The cells were then cycled for a short period (one full cycle) and stopped at an open circuit voltage of 3.775 V corresponding to approximately 50% state of charge. The electrochemical impedance spectra of the cells were then taken at 10 °C, 20 °C, 30 °C, and 40 °C. Then the cells were taken inside an argon-filled glove box for disassembly and construction of symmetric cells from their electrodes as described in Ref. [12].

The cells were carefully opened in an argon filled glove box. From the long doubled-sided electrodes, 9 coin-cell size (1.54 cm²) positive electrodes and 9 coin-cell size negative electrodes were cut with a precision punch. From the punched (double sided) electrodes, 3 full coin cells, 3 negative symmetric coin cells and 3 positive symmetric coin cells were reassembled using one polypropylene blown microfiber separator (BMF – available from 3M Co. 0.275 mm thickness, 3.2 mg cm⁻²) [13] and the same electrolyte formulation as the parent prismatic wound cells. A full cell is constructed using one positive electrode and one negative electrode, a positive symmetric cell is constructed using 2 positive electrodes, and a negative symmetric cell is constructed using 2 negative electrodes.

The EIS spectra of the reassembled coin cells were then recorded at 10 °C and 30 °C in that order. All EIS spectra were taken using a BioLogic VMP3 equipped with 2 EIS boards. Many EIS spectra were collected over the course of these experiments and in order to automate the process somewhat, the output of one VMP3 EIS board was connected to a Keithley 705 scanner and the output of the other to a Keithley 706 scanner. Each scanner housed two Keithley 7053 10-channel high current scanner cards. In-house software was designed and written so that each scanner could connect up to 16 cells sequentially to have their EIS spectra measured automatically overnight. All impedance spectra were collected at constant temperature by housing the cells in temperature-controlled boxes at 10.0 and 30.0 ± 0.2 °C.

3. Results and discussion

As shown in Ref. [12] the impedance of the positive symmetric cells grows over time, whereas the impedance of the full cells and negative symmetric cells are stable. This indicates the existence of an interaction between the positive and negative electrodes in the full cell that somehow prevents the impedance of the positive electrode from growing. It also suggests the existence of an autocatalytic reaction when the 2 positive electrodes are in the same

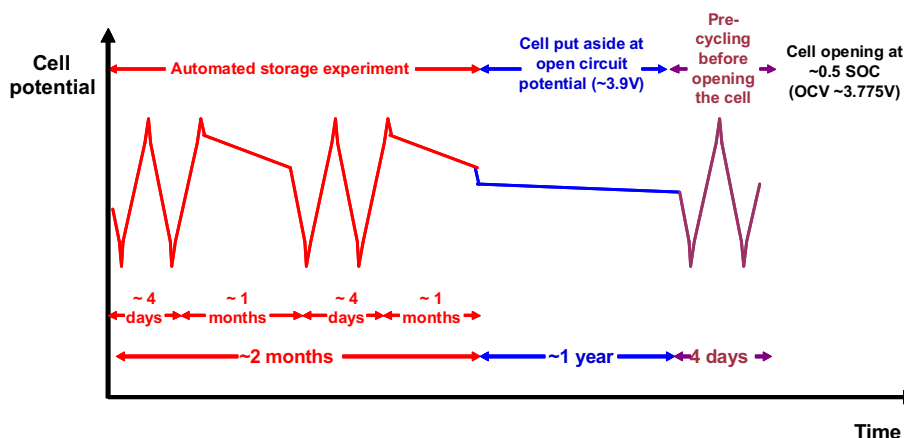


Fig. 1. Schematic of the history of the wound prismatic cells used for the “EIS on symmetric cells study”.

cell that is somehow inhibited when the graphite electrode is present. Since the positive electrode impedance grows over time and that there is a significant delay between the positive symmetric cell assembly and the impedance measurement, the positive symmetric cell impedance was calculated from the full cell impedance and the negative symmetric cell impedance. Some electrolyte additives dramatically slowed the increase of the impedance of the positive electrode symmetric cells with time, and in these cases the calculated impedance agreed well with the measured impedance. Equation (1) presents the expression for the calculated impedance of the positive symmetric cell, where $Z_{(+/+)}$ is the impedance of the positive symmetric cell, $Z_{(-/-)}$ is the impedance of the negative symmetric cell, and $Z_{(+/-)}$ is the impedance of the full cell.

$$Z_{(+/+)} = 2 \left(Z_{(+/-)} - \frac{Z_{(-/-)}}{2} \right) \quad (1)$$

Fig. 2 presents the equivalent circuit model proposed by Atebamba et al. [14] used to fit the impedance spectrum of the negative symmetric cells and the calculated spectrum of the positive symmetric cells. The model consists of three main components. The first component is the electrolyte series resistance represented by R_{el} . The second is the contact resistance between the active particle and the current collector, and associated capacitance (constant phase element) represented by R_{cr} and C_{cr} respectively. The third component comprises the charge transfer resistance of the Li ions through the SEI, in series with a Warburg resistance (representing the solid state diffusion of Li in the active particles), and an associated double layer capacitance (constant phase element) represented by R_{ct} , W and C_{ct} respectively.

Fig. 3 presents half of the area specific impedance of a positive symmetric cell (a) and of a negative symmetric cell (b) along with the calculated impedance spectra using the Atebamba et al. [14] model. The model parameters of the calculated spectra were

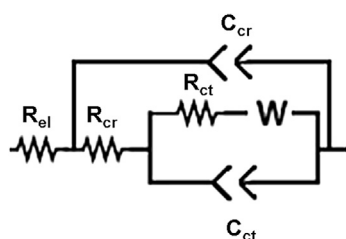


Fig. 2. Schematic of the equivalent circuit model proposed by Atebamba et al. [14] used to fit the electrochemical impedance spectra of the negative symmetric cells and the calculated electrochemical impedance spectra of the positive symmetric cells.

adjusted to give the best fit between experiment and calculation in a least-squares sense. Fig. 3 shows a very good agreement between the electrochemical impedance spectra and the calculated spectra using the equivalent electrochemical circuit model shown in Fig. 2. Since a change in the chemical structure of the SEI changes R_{ct} of an electrode, comparing the value of the charge transfer resistance of the positive electrode and the negative electrode of cells containing different additives to the charge transfer of the electrodes of a cell containing no additive allows assessing at which electrode this additive acts.

Fig. 4 presents the charge transfer resistance of the positive electrode of NMC cells (a, b), LV-LCO cells (c, d) and HV-LCO cells (e, f) at 10 °C (a, c, e) and 30 °C (b, d, f) obtained by fitting the inferred electrochemical impedance spectra of the reassembled positive symmetric cells ($(+/+) = 2(+/+) - (-/-)$) using the equivalent circuit model in Fig. 2. Fig. 4 shows that all additives and additive combinations used affected the positive electrode surface in all cell chemistries studied (NMC/graphite, LV-LCO/graphite, and HV-LCO/graphite). Almost every additive used reduced the charge transfer

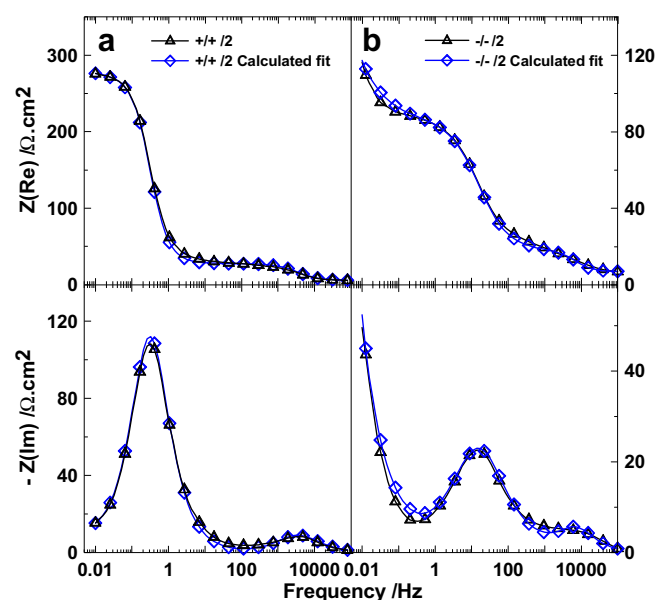


Fig. 3. Bode representation of the calculated area specific impedance of a positive symmetric cell and its fit (a), and area specific impedance of a negative symmetric cell and its fit (b), using the Atebamba et al. model [14].

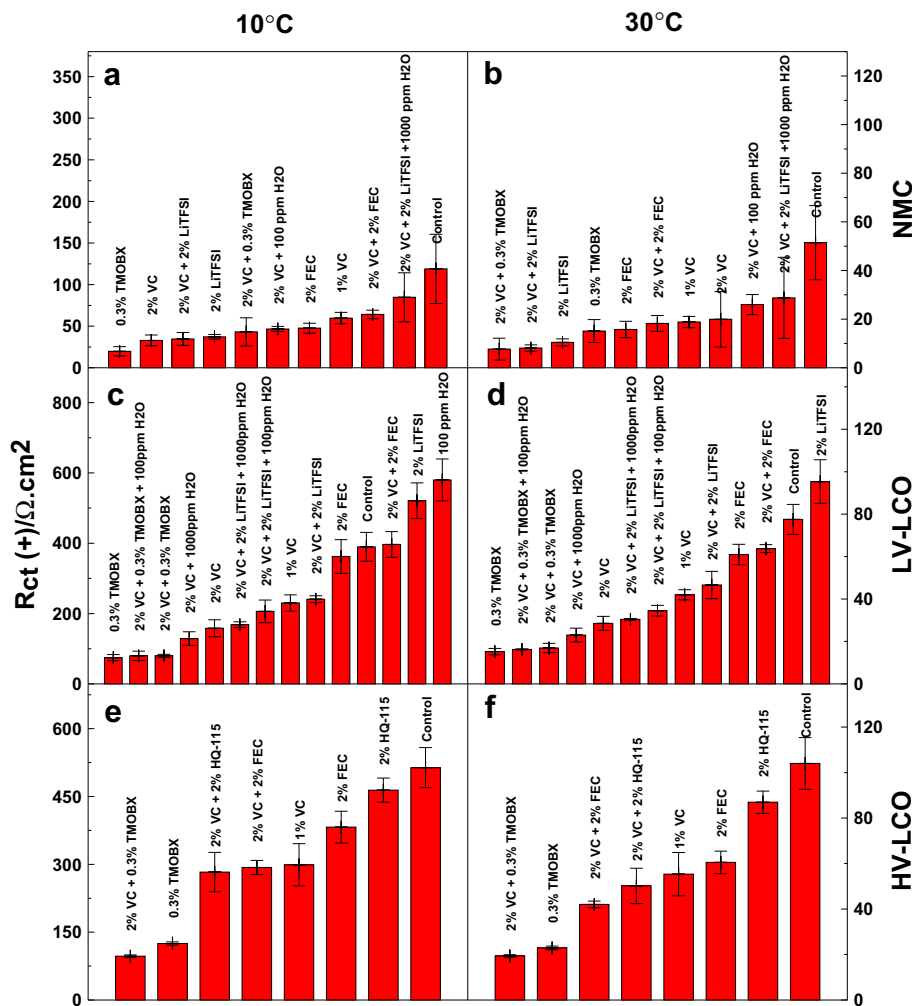


Fig. 4. Charge transfer resistance of the positive electrode of NMC cells (a, b), LV-LCO cells (c, d), and HV-LCO cells (e, f) at 10 °C (a, c, e) and 30 °C (b, d, f) obtained by fitting the calculated area specific electrochemical impedance spectra of the positive symmetric cells using the equivalent circuit proposed by Atebamba et al. [14].

impedance of the positive electrode with the exemption of H₂O and LiTFSI when used alone in the LV-LCO cells. Fig. 4 shows that TMOBX is an effective additive for reducing the charge transfer resistance at the positive electrode in all the cell chemistries as stated in earlier publications [3,12].

Fig. 4 also helps determine which additive controls the surface chemistry at the positive electrode when more than one additive is included in the electrolyte. For instance, when VC and TMOBX are added in LV-LCO and HV-LCO cells, the value of the R_{ct} at the positive electrode is the same as for TMOBX alone. This suggests that TMOBX controls the surface chemistry of LCO electrodes when mixed with VC. The error bars for R_{ct} for the mix of TMOBX and VC in NMC cells do not allow one to suggest which additive is controlling the surface chemistry. Fig. 4a and c shows that LiTFSI has a different effect on the positive electrode surface of NMC cells, LV-LCO cells, and HV-LCO cells. Adding LiTFSI to NMC cells reduces significantly R_{ct} compared to control, adding LiTFSI to HV-LCO cells reduces slightly R_{ct} of the positive electrode and adding LiTFSI to LV-LCO cells increases R_{ct} of the positive electrode. This might indicate a dependence of the effect of LiTFSI on the type of positive material used or on the potential to which the cells were exposed. R_{ct} of the positive electrode of the HV-LCO and LV-LCO cells containing 2% LiTFSI are the same. It seems like LiTFSI keeps the SEI of the positive electrode unchanged when the higher voltage cut-off is increased.

Based on Fig. 4c and d, both LiTFSI and VC affect the positive electrode surface chemistry when introduced together in LCO cells. The similarity of the impact of LiTFSI and VC on R_{ct} of the positive electrode of the NMC cells does not allow one to distinguish which additive controls the surface chemistry of the positive electrode when both additives are present. Fig. 4a, c and d shows that FEC and VC have different impacts on R_{ct} of the positive electrode of NMC cells and LV-LCO cells (2% VC in HV-LCO cells were not available). This indicates that the effects of FEC and VC at the positive electrode are different.

Fig. 4 shows that adding 100 ppm of H₂O to NMC and LV-LCO cells containing VC, TMOBX, VC + TMOBX, VC + LiTFSI affects R_{ct} slightly indicating that VC, TMOBX, LiTFSI, and their combination control most of the surface chemistry of NMC and LCO electrodes when only 100 ppm of H₂O is introduced. Adding 1000 ppm of H₂O to NMC and LV-LCO cells containing VC, and VC + LiTFSI affects R_{ct} significantly indicating that H₂O participates in the formation of the SEI at the positive electrode when a larger concentration is introduced. Every wound cell containing H₂O used in this study showed a brownish color on the separator once they were opened and had an unusually bad adhesion of the negative electrode to the copper foil. The adhesion of the positive electrode to the current collector was not altered by the addition of H₂O (compared to cells containing other additives), except for the cell containing 2% VC and 100 ppm H₂O.

Fig. 5 shows the charge transfer resistance of the negative electrode of NMC cells (a, b), LV-LCO cells (c, d) and HV-LCO cells (e, f) at 10 °C (a, c, e) and 30 °C (b, d, f) obtained by fitting the electrochemical impedance spectra of the reassembled negative symmetric cells using the equivalent circuit model presented in Fig. 2. Fig. 5 shows that all additives used increased R_{ct} of the negative electrode, except for LiTFSI, which did not show any significant effect at the negative electrode of LV-LCO cells and HV-LCO cells. LiTFSI appears to have reduced the impedance of the negative electrode of NMC cells. Except for LiTFSI-containing cells, the value of R_{ct} of the negative electrode of NMC cells, LV-LCO cells and HV-LCO cells containing the same electrolyte formulation are very similar. This indicates that the positive electrode material and upper voltage cut-off (in the voltage range studied) do not have any significant effect on the surface of the negative electrode. As indicated in an earlier publication [5,12] varying the concentration of VC from 1 wt% to 2 wt% has a great impact on R_{ct} of the negative electrode without improving the coulombic efficiency or the voltage drop during an automated storage experiment. As a consequence, introducing a large amount of VC will have a negative impact on the rate capability of a cell. Fig. 5 shows that TMOBX affects the surface of the negative electrode slightly. When VC and TMOBX are introduced in the same cell, R_{ct} of the negative electrode is the same as for cells containing VC only, indicating that VC

controls the surface chemistry of the negative electrode over TMOBX.

Fig. 5 also shows that FEC and VC have different effects on R_{ct} of the negative electrodes. FEC caused a greater R_{ct} at the negative electrode than VC did. This indicates that the SEI at the negative electrode that FEC creates is different from the one that VC does. Fig. 5c shows that H₂O does not have any significant impact on the R_{ct} of the negative electrode when introduced alone. Fig. 5a–f shows that the effect of FEC on the negative electrode surface prevails when introduced with VC.

Fig. 5a–d shows that introducing H₂O to cells containing VC, VC and LiTFSI, VC and TMOBX reduces R_{ct} of the negative electrode. This indicates that H₂O modifies the nature of the SEI of the negative electrode of cells containing VC, LiTFSI, and TMOBX. It also indicates that the electrode which H₂O affects depends on the additive added to the cell and points towards an interaction between H₂O and the by-products of the degradation of other additives.

Fig. 6 shows side by side the R_{ct} of the positive electrode (a, b) and negative electrode (c, d) of LV-LCO cells and HV-LCO cells. This figure helps to determine the effect, if any, of a higher cut-off potential on the effects of additives. For instance, Fig. 6a and b shows that the positive electrode of cells containing no additive, 1% VC, 2% VC and 0.3% TMOBX have a higher R_{ct} when charged to a higher cut-off voltage. This is not surprising and is expected since a higher

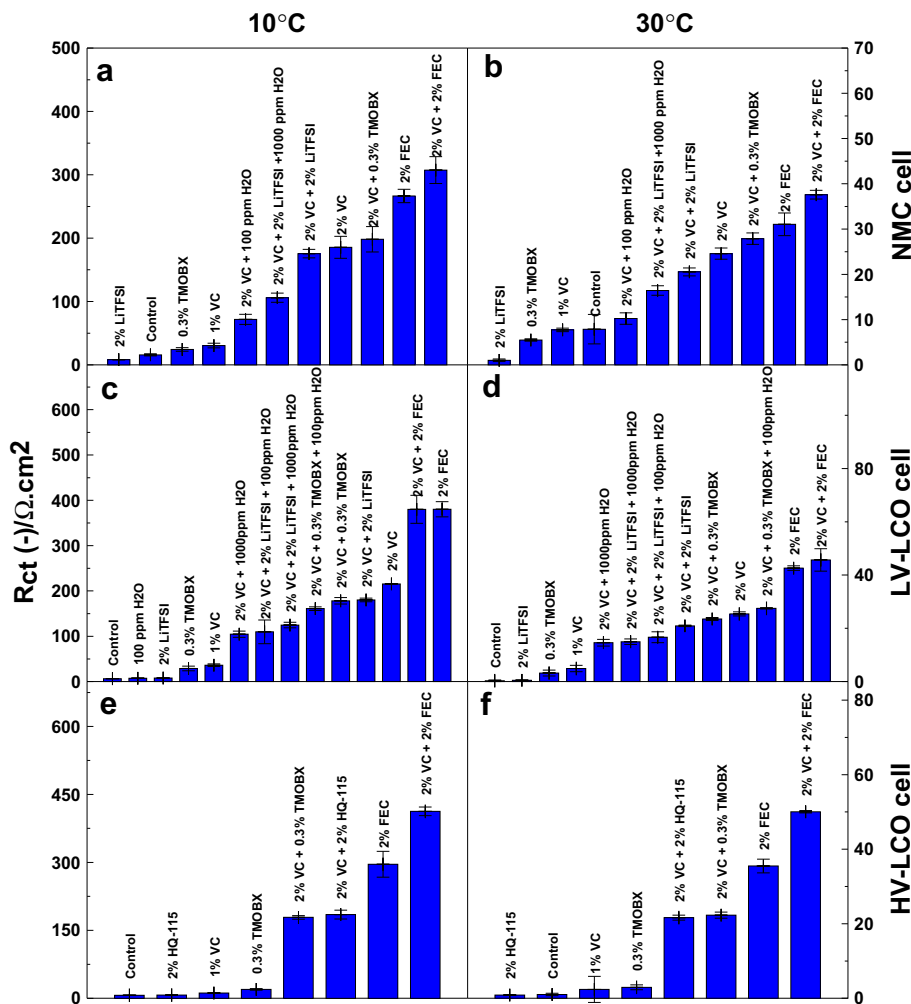


Fig. 5. Charge transfer resistance of the negative electrode of NMC cells (a, b), LV-LCO cells (c, d), and HV-LCO cells (e, f) at 10 °C (a, c, e) and 30 °C (b, d, f) obtained by fitting the area specific electrochemical impedance spectra of the negative symmetric cells using the equivalent circuit proposed by Atebamba et al. [14].

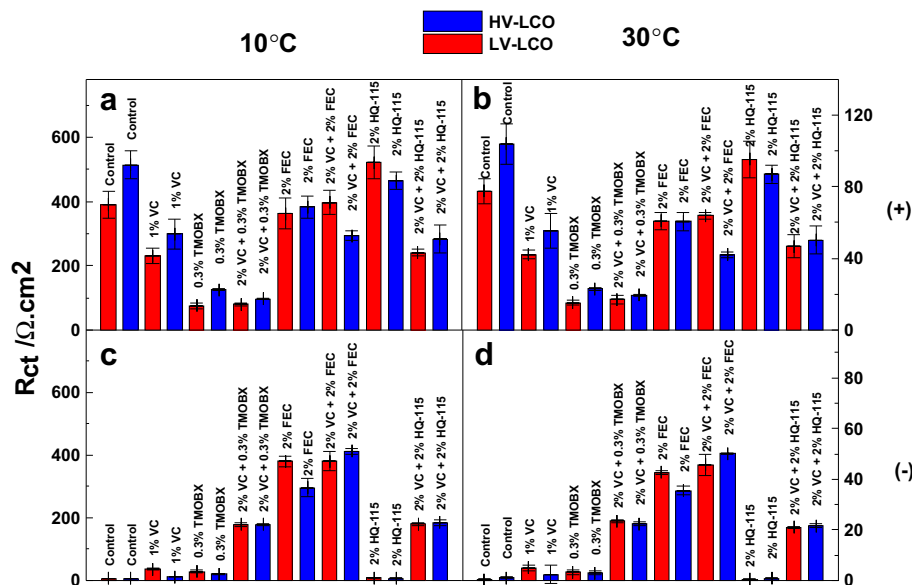


Fig. 6. Comparison of the charge transfer resistance of the positive electrode of LV-LCO (red) and HV-LCO cells (blue) at 10 °C (a) and 30 °C (b) and the charge transfer resistance of the negative electrode of LV-LCO (red) and HV-LCO cells (blue) at 10 °C (c) and 30 °C (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

voltage promotes electrolyte oxidation at the positive electrode from which reaction by-products can form at the surface of the electrode. However, cells containing 2%VC + 0.3% TMOBX, 2% FEC, 2% LiTFSI, 2% VC + 2% LiTFSI do not have a higher R_{ct} when charged to higher voltage. This suggests that for these cells the SEI of the positive electrode does not change when the voltage cut-off is increased by 100 mV near 4.1 V. However this does not necessarily indicate a reduction in the rate of electrolyte oxidation as the by-products can be soluble and not participate in the thickening of the SEI. Cells containing 2% VC + 2% FEC have a lower R_{ct} at the positive electrode when the cell is charged at a higher voltage cut-off. This may indicate the creation of a slightly different SEI when the cell is charged at a different cut-off.

Fig. 6c and d shows that R_{ct} of the negative electrode of HV-LCO cells is very similar to R_{ct} of the negative electrode of LV-LCO cells containing the same electrolyte formulation, with the exception of cells containing 2% FEC and 1% VC. It seems like for most of the cells studied, the difference in the higher cut-off voltage (in the range used) does not influence the SEI of the negative electrode.

Fig. 7 shows the coulombic inefficiency (CIE) during cycling on a high precision charger [15] (a, c, e) and the voltage drop during automated storage experiments (b, d, f) for wound prismatic LV-LCO cells, HV-LCO cells, and NMC cells containing different electrolyte additives and additives mixes. The CIE data were collected during C/20 cycling at 40 °C and are reported for the average of the 14th to 16th cycles of all cells. The cells used in the automated storage experiments are the same cells used for the EIS on symmetric cells study. The data for the cells containing no additive, TMOBX, VC, and LiTFSI shown in Fig. 7 were already presented in earlier publications [3,5]. The voltage drop during the automated storage experiment measures the rate of parasitic reactions at the positive electrode [7,8], the greater the voltage drop, the greater the rate of the parasitic reactions at the positive electrode. Normally, cells with the longest cycle life have the smallest CIE.

Fig. 7 allows some general comments to be made on the effect of an additive on the cycling behavior of a cell. Compared to control, the addition of either VC (1 wt% and 2 wt%), or 2 wt% FEC reduces the CIE (good) and the voltage drop (good) for both cell chemistries

(NMC and LCO) which indicates a reduction in the parasitic reactions between the electrodes and the electrolyte. Compared to control, the addition of LiTFSI reduces the CIE slightly (good) but does not have any significant impact on the voltage drop (neutral) for both NMC and LCO cells. Compared to control, the addition of TMOBX reduces the CIE (good) and doesn't have any impact on the voltage drop (neutral) of LV-LCO cells, reduces the CIE (good) and increases the voltage drop (bad) of HV-LCO cells, and increases the CIE (bad) and voltage drop (bad) of the NMC cells. This suggests that the effect of the addition of TMOBX worsens (in terms of parasitic reactions at the positive electrode) as the voltage cut-off of the cell is increased from 4.075 to 4.175–4.225 V.

Fig. 7 shows that compared to control, 100 ppm of H₂O increases somewhat the CIE and voltage drop of NMC and LV-LCO cells. Adding 2% LiTFSI to 2% VC does not seem to have any noticeable impact on the cycling performances of all cell chemistries compared to VC by itself. Adding 0.3% TMOBX to 2% VC increases the CIE of LV-LCO and HV LCO, doesn't have any noticeable effect on the CIE of the NMC cells, and increases the voltage drop of all cell chemistries. However, the CIE and voltage drop of VC + TMOBX cells are still significantly lower than the control cells. Adding 100 ppm H₂O to 2% VC improves the CIE of the NMC cells but does not have any noticeable effect on the CIE of LV-LCO cells, and increases the voltage drop of both NMC and LV-LCO cells. Compared to 2% VC + 100 ppm H₂O, 2% VC + 1000 ppm H₂O improves the CIE slightly and reduces the voltage drop (the voltage drop is still higher than 2 wt% VC by itself). Adding 100 ppm H₂O to 2% VC + 2% LiTFSI increases the CIE and voltage drop of NMC and LCO cells. Compared to 2% VC + 2% LiTFSI + 100 ppm H₂O, increasing the concentration of H₂O to 1000 ppm reduces the CIE (CIE is even lower than 2% VC + 2% LiTFSI) and voltage drop of both NMC cells and LV-LCO cells (V-drop is still higher than 2% VC + 2% LiTFSI). Adding 100 ppm of H₂O to 2% VC + 0.3% TMOBX reduces the CIE and leaves the voltage drop unchanged for LV-LCO cells.

Combining the information contained in Figs. 4–7 allows one to make some conclusions about the properties of the additives studied. For example, TMOBX does not have any beneficial effect in terms of CIE and voltage drop for cells operating at high voltage, if anything, it makes it worse. The only advantage of using TMOBX

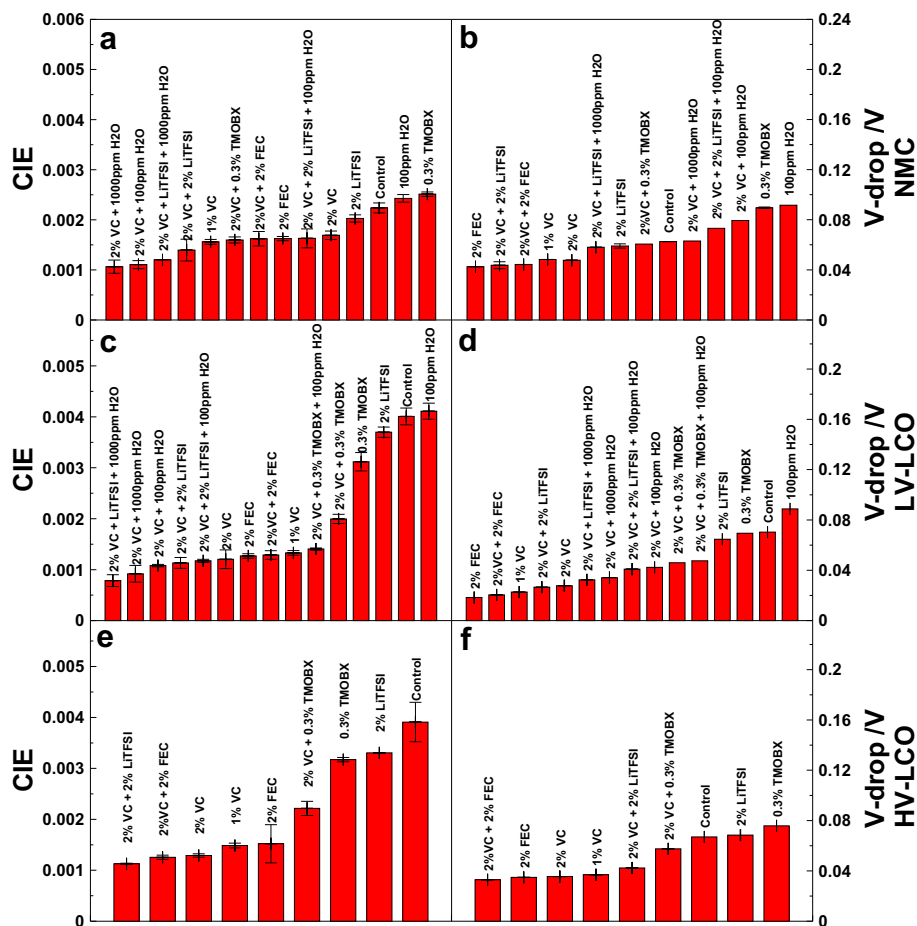


Fig. 7. Coulombic inefficiency (a, c, e) and voltage drop (b, d, f) during cycling on a high precision charger and automated storage experiments for NMC/Graphite cells charged to 4.225 V (a, b), LCO/Graphite cells charged to 4.075 V (c, d), and LCO/Graphite cells charged to 4.175 V (e, f).

alone would be for the reduction of the impedance. From the EIS on symmetric cells study, this impedance reduction comes from the SEI at the positive electrode that TMOBX creates. VC and FEC have the same effect on the CIE and voltage drop of all tested cells (they reduce them both) imparting a good cycle life to the cell. From the EIS study on symmetric cells, VC and FEC act both at the positive and negative electrodes but create different SEIs. VC might be more advantageous than FEC due to smaller charge transfer resistances at both the negative and positive electrodes compared to FEC.

LiTFSI brings minor improvements to the CIE and voltage drop (does not slow down the parasitic reactions significantly). From the EIS on symmetric cell study, LiTFSI has no effect at the negative electrode and some effect at the positive electrode. From these results, LiTFSI is a good additive for lowering the charge transfer resistance of the positive electrode of cells used at high voltage. Adding LiTFSI to 2% VC does not have any strong impact on the CIE and voltage drop of all tested cells. From the EIS study, VC controls the formation of the SEI at the negative electrode and both LiTFSI and VC control the SEI at the positive. However compared to VC, the modification of the SEI at the positive produced by the addition of LiTFSI does not affect the reduction of the rate of the parasitic reactions that VC creates.

Adding 2% FEC to 2% VC does not have any impact on the CIE and the voltage drop of the cells. This is not surprising since FEC and VC have exactly the same effect when introduced separately in these cells. When VC and FEC are added together, FEC seems to control the formation of the SEI at the negative electrode and both FEC and

VC seem to control the SEI at the positive electrode. As a consequence, adding FEC to VC does not bring any improvement in these cells, and worsens R_{ct} at both electrodes, reducing the power capability of the cell.

Adding 0.3% TMOBX to 2% VC increases the CIE and voltage drop slightly. However it decreases the R_{ct} of the positive electrode and leaves the R_{ct} of the negative electrode unchanged. This indicates that the SEI at the positive electrode TMOBX creates is responsible for the increase of the rate of the parasitic reactions. From the EIS study, TMOBX controls the formation of the SEI at the positive electrode and VC controls the formation of the SEI at the negative electrode.

Adding 100 ppm of H_2O to control cells worsens the cycle behavior of LV-LCO cells and NMC cells. Based on the EIS study, it seems like most of the effects of H_2O (when introduced alone) are at the positive electrode. Adding 100 ppm of H_2O to 2% VC + 0.3% TMOBX improves the CIE and does not have any significant effect on the voltage drop. From the EIS study, it seems like H_2O modifies the SEI at the negative electrode and leaves the SEI at the positive electrode unchanged. This is somewhat expected since the voltage drop is unchanged with the addition of H_2O . Adding 100 ppm of H_2O in 2% VC cells, and 2% VC + 2% LiTFSI improves the CIE somewhat and increases the voltage drop. However, adding 1000 ppm of H_2O to the 2% VC, and 2% VC + 2% LiTFSI cells improves the CIE even more and reduces the voltage drop. From the EIS study on LV-LCO cells, adding 100 ppm of H_2O to 2% VC, and 2% VC + 2% LiTFSI has a slight impact on the positive electrode and a great

impact (reduces the R_{ct}) on the negative electrode. Adding more H_2O to the 2% VC + 2% LiTFSI seems to have a greater effect on the positive electrode than on the negative electrode. This indicates a complex reactivity of H_2O . The electrode that H_2O affects depends on both the additives added with it, along with its own concentration.

4. Conclusions

The study of electrolyte additives using the EIS on symmetric cells method described in an earlier publication allowed studies of the effect of several additives and additive combinations on the positive and negative electrodes separately to be made. Combining this study with high precision coulometry and automated storage experiments allowed an assessment of the effect of additives on the cycling performances of NMC/graphite and LCO/graphite cells along with determining on which electrode they act. Being able to correlate cycling behavior to the effect of an additive on each electrode helps to shed light on the complicated mechanisms involved in the way additives work.

This study showed that the behavior of an additive depends on the presence or absence of other additives and that in some cases some additives control the formation of the SEI at the positive electrode, or the negative electrode, or both. For example, VC controls the formation of the SEI at the negative electrode when introduced with LiTFSI and TMOBX but not with FEC. TMOBX controls the formation of the SEI at the positive electrode when introduced with VC.

This study also showed that the effect of varying the concentration of an additive does not always result in additive behavior. For instance, increasing the concentration of VC from 1 wt% to 2 wt % resulted in an unexpected increase of the negative electrode impedance. Also, adding 100 ppm of H_2O in cells containing VC affected the negative electrode more than the positive electrode,

but introducing 1000 ppm of H_2O had a greater impact on the positive electrode than on the negative electrode.

This study shows that to get good cycling performances (low CIE, voltage drop and impedance) additives must be used. The ideal additive or additive combination should help create SEI layers at both the positive and negative electrodes that have low charge transfer resistance and that slow down the parasitic reactions.

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